

NOTICE: When government or other drawings, specifications or other data are used for any purpose other than in connection with a definitely related government procurement operation, the U. S. Government thereby incurs no responsibility, nor any obligation whatsoever; and the fact that the Government may have formulated, furnished, or in any way supplied the said drawings, specifications, or other data is not to be regarded by implication or otherwise as in any manner licensing the holder or any other person or corporation, or conveying any rights or permission to manufacture, use or sell any patented invention that may in any way be related thereto.

Abstract for Symposium on Inorganic Chemistry of Electrically Active Solids,
American Chemical Society Meeting, Miami, April 7-11, 1957.

(5) 689 105
Crystal-Chemical Mechanisms in
Ferroelectrics and Antiferroelectrics*

(10) Ray Pepinsky
X-Ray and Crystal Analysis Laboratory
Department of Physics
The Pennsylvania State University
University Park, Pa.

60. 6. 1957
TISA B

AD 419119
DDC 419119
AD 419119
DDC 419119
Studies of the structures and transition mechanisms of ferroelectric crystals are important not merely because knowledge of these facilitates the discovery of new ferroelectrics, but because they shed much light on the larger problems of the nature and interplay of bonding forces in crystals, and the stability of structures.

At the present writing the following classes of ferro- or anti-ferroelectrics are well established: (1) the perovskites (e.g., BaTiO_3) and several other oxygen-octahedra types ($\text{Cd}_2\text{Nb}_2\text{O}_6$, $\text{Cd}_2\text{Nb}_2\text{O}_7$, etc.); (2) the KH_2PO_4 and $\text{NH}_4\text{H}_2\text{PO}_4$ family; (3) the tartrates ($\text{NaKC}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$, $\text{LiNH}_4\text{C}_4\text{H}_4\text{O}_6 \cdot \text{H}_2\text{O}$, and others); (4) $(\text{NH}_4)_2\text{SO}_4$ and isomorphs; (5) $(\text{NH}_4)_2\text{Cd}_2(\text{SO}_4)_3$; (6) guanidinium $\text{Al}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ and isomorphs; (7) many NH_4 , hydrazine, hydroxylamine and organic amine alums; (8) the para-periodate antiferroelectrics; (9) glycine sulfate and isomorphs; (10) colemanite; and (11) thiourea.

Through x-ray and neutron diffraction studies, crystal-chemical mechanisms are now fairly well known for the dielectric behavior of some

members of groups (1) and (2). The most pressing problem remaining, in these groups, is need for understanding of the effects of isomorphous replacement. In (3), mechanisms in several types of tartrates are still mysterious. The large involvement of one of the central OH groups of the tartrate ion, in the spontaneous polarization of Rochelle Salt, is now clear from a neutron study; but the behaviors of the LiNH_4 , LiTl and $\text{Na}(\text{K},\text{NH}_4)$ tartrates remain unexplained as yet.


The structures of families (6) and (7) are somewhat related; but the dielectric behavior of the two families probably arises from quite different mechanisms. The structure of a representative member of (6) has been determined, and a conjecture is offered concerning the polarization mechanism. As to (7): the long-accepted α and β alum structures are in great need of revision, and this is particularly true of the organic amine alums. These structures are again under study. In methylammonium aluminum alum, beautiful x-ray evidence is available of hindered rotation of the $(\text{CH}_3\text{NH}_3)^{+1}$ ion above the Curie point; and ferroelectric behavior is doubtlessly associated with ordering of this ion.

Ammonium ion rotations are certainly involved in groups (4) and (5), but these must be confirmed and details of consequent structural changes established via neutron diffraction analyses. $(\text{NH}_4)_2\text{SO}_4$ is now under neutron examination. No mechanisms have been discussed, as yet, for groups (8), (10) and (11). Thiourea is the first non-ionic ferroelectric; its transitions are also under neutron study.

The basic features of the mechanism in the $(\text{glycine})_3 \cdot \text{H}_2\text{SO}_4$ system,

(9), is revealed by consideration of chemical and symmetry properties alone. From these, it is clear that the compound is a chemical anomaly, and that most amino acids cannot form isomorphous crystals. The complete paraelectric structure has now been elucidated. The effects of isomorphous replacement of the inorganic ion (by SeO_4^{-2} or BeF_4^{-2}) on the transition temperature and coercive field can be qualitatively explained.

New ferroelectrics are being discovered far faster than their structural mechanisms can be elucidated. Several new systems of antiferroelectrics have also appeared, and others are suspected to exist. Nevertheless, out of the large numbers of crystals showing transitions, ferro- and antiferroelectric activity is still rare. It is possible to explain, to some extent, why this is the case.

 *Research supported by ~~Contracts No. AF18(603)-35, with the~~ Air Force Office of Scientific Research, No. DA36-039-SC-63233 with the Signal Corps Engineering Laboratories, and No. AT(30-1)-1516 with the Atomic Energy Commission, and by Brookhaven National Laboratory.